

DEGRADATION OF Fe-Mg SILICATES IN HOT CO₂ ATMOSPHERES: APPLICATIONS TO VENUS

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Introduction. When basaltic magma extrudes onto the surface of a terrestrial planet, the crystallizing ferromagnesian silicates may interact with the atmosphere as the minerals cool down causing changes of oxidation state and mineralogy of iron. On Earth during the Archean and continually on the surfaces of Mars and Venus, hot olivine and pyroxenes in basalt lava flows were exposed to CO₂-dominated atmospheres, causing Fe²⁺ ions to be vulnerable to weathering reactions. Under present-day conditions on the Venusian surface, chemical weathering is occurring on lowlands [1,2] at temperatures of ~450-475 °C and pressures of ~90-100 bars in an atmosphere of ~97 vol. % CO₂. Under these conditions, degradation of primary igneous minerals is predicted from equilibrium thermodynamic calculations [e.g., 3-6]. However, comparatively few experimental measurements have been made to verify chemical weathering reactions of minerals in hot CO₂-dominated atmospheres [1]. Preliminary experiments of powdered igneous rocks heated in CO₂ produced darkening [7] tentatively attributed to the oxidation of iron-bearing minerals in the rocks to magnetite, which was predicted to be the stable form of iron on the Venusian surface [1,2,8]. However, hematite was suggested to be present in darkened basaltic surfaces of Venus, based on correlations of multispectral images of the Venera 9 landing site and high temperature laboratory reflectance spectra of basaltic materials [9]. Such conflicting information lead to measurements described here of olivine and pyroxenes heated in CO₂ atmospheres, extending recent investigations of products of aerial oxidation of Fe²⁺-bearing olivines [10] and pyroxenes [11] heated in Earth's atmosphere.

Experimental Details. Minerals heated in CO₂ included olivine (Fa₄₉), orthopyroxene (Fs₂₉), augite (Wo₄₇Fs₁₀En₄₆), Mn-hedenbergite (Wo₅₀Fs₄₀Mn₁₀), stoichiometric magnetite (Fe²⁺Fe³⁺₂O₄), and crystalline hematite (Fe₂O₃). Powdered samples (particle diameters < 45 microns) were heated at 790 °C (olivine) or 800 °C (pyroxenes, oxides) for 1-28 days in a muffle furnace under continuously flowing CO₂ (containing 30 ppm O₂) at slow (0.25 ml/sec) or fast (3.0 ml/sec) flow-rates. The Mössbauer spectra of the products from the CO₂-degradation experiments were measured at room temperature, 77K and 4.2K to identify structural Fe²⁺ and Fe³⁺ ions in the minerals and nanophase ferric oxides formed by oxidation. Comparisons were made with the spectral profiles of the oxidized minerals obtained from high temperature aerial oxidation measurements described previously [10,11].

Results. Magnetite and Hematite. In one-day experiments at 800 °C, hematite remained unchanged when heated in CO₂. The magnetite became non-stoichiometric and was partially converted to hematite.

Olivine. In a 6-day experiment performed in CO₂ at 790 °C by Bruce Fegley, almost 80% of the Fe²⁺ in olivine was oxidized to hematite. The oxidation product yielded a magnetic hyperfine spectrum at 295K indicative of "crystalline" hematite instead of superparamagnetic (nanophase) Fe₂O₃ which was encountered previously in aerially oxidized [11] and the CO₂-degraded pyroxenes described below.

Orthopyroxene. The ferric iron initially present in the unheated orthopyroxene (~7.5% Fe³⁺) increased rapidly to ~18.5% after heating in CO₂ for 7 days and levelled off at ~22.5% after 4 weeks. The 295K and 77K Mössbauer spectra showed negligible amounts of magnetically-ordered Fe₂O₃. However, by 4.2K a hematite sextet had appeared accounting for some of the ferric iron. Thus, some nanophase hematite with particle sizes ≤4 nm [12,13] had been formed by oxidation of Fe²⁺ in orthopyroxene, in contrast to earlier aerial oxidation experiments

in which almost 50% of the ferrous iron was oxidized to nanophase hematite in runs performed at similar temperatures and time periods [11].

Pigeonite. After heating pigeonite in CO₂, the hematite sextet was prominent in the 295K Mössbauer spectrum together with Fe²⁺ and Fe³⁺ doublets, indicating that ferrous iron in this pyroxene is particularly vulnerable to oxidation.

Augite. In the unheated pyroxene, ~26% of the iron occurs initially as structural Fe³⁺ ions. After heating in CO₂ for 7 days, ferric iron increased to 42% and levelled off at ~50% after 4 weeks. No ferric oxide sextet appeared in the 4.2K Mössbauer spectrum of the oxidized augite.

Hedenbergite. The 4.3% ferric iron initially present in the hedenbergite increased to ~33.3% after heating in CO₂ for 2 weeks. A magnetic sextet attributable to hematite appeared in the 4.2K Mössbauer spectrum together with a poorly defined ferric sextet attributed to structural Fe³⁺ ions. Similar results were obtained previously for hedenbergites heated in Earth's atmosphere [11].

Discussion. The experiments demonstrate that oxidation of ferromagnesian silicates and magnetite occurs when these minerals are heated at 800 °C in 1 atmosphere of CO₂, under which conditions hematite is thermodynamically stable [14]. The 30 ppm oxygen impurity in the CO₂ presumably facilitates the oxidation of some of the ferrous iron initially present in the crystal structures of the minerals. The Mössbauer spectral measurements reveal, however, that only in CO₂-degraded olivine and pigeonite is hematite formed as a magnetically-ordered phase at ambient temperatures. In orthopyroxene, some of the ferric iron produced by oxidation is present as nanophase hematite which, because it remains superparamagnetic until 4.2K, must exist as particles ≤ 4 nm in diameter. In the calcic pyroxenes, however, much of the oxidized ferrous iron may still remain as structural Fe³⁺ in the host silicates. Some ferric iron may also be present as unit-cell sized Fe₂O₃ inclusions in the pyroxenes, or be segregated along cleavage planes, or be coating mineral grains. In these states of aggregation, the Fe₂O₃ is unidentifiable by X-ray diffraction and in low temperature Mössbauer spectra.

Applications to Venus. The temperatures used in the CO₂-degradation experiments are considerably higher than those encountered on the present-day surface of Venus. However, the lower partial pressure of CO₂ used in the experiments and the inherent impurity of oxygen may be compensatory, by analogy with reactions involving SO₂-CO₂ gas mixtures [15]. Although equilibrium calculations predict an oxygen mole fraction of ~10⁻²⁴ in the near-surface troposphere of Venus [2,8], published results obtained from the Venera 13 and 14 space missions [17] show the presence of ~18 ppm O₂. Therefore, the 30 ppm O₂ present in the 1 atmosphere CO₂-degradation experiments described here may, in fact, be *less* oxidizing than conditions existing in the high pressure atmosphere on Venus. Certainly, the positive identification of hematite, and not magnetite, as the oxidation product of olivine, pigeonite, hedenbergite and, perhaps, orthopyroxene after being heated in CO₂ correlates with observations from multispectral imaging [9] indicating that Venus has a highly oxidized surface [2].

The presence of hematite on Venus is also consistent with the normative mineralogy calculated from analyses of surface rocks at the Vega 2 landing site [18]. The *in situ* XRF analysis reported the iron as 7.7 ± 1.1 wt. % FeO [18]. Assuming that all of the iron is in the ferrous state, CIPW norm calculations [19] yield 26% orthopyroxene, 10% olivine, 3% calcic clinopyroxene and zero percent hematite or magnetite [20]. If, however, the assumption is made that there are equi-molecular proportions of FeO and Fe₂O₃ in the XRF analysis, the computed normative mineralogy corresponds to 31% orthopyroxene, 3% calcic clinopyroxene, 5% hematite, 1% magnetite and zero percent olivine. This mineral assemblage is consistent with the experimental evidence that heated olivines are most vulnerable to oxidation in CO₂-dominated and terrestrial atmospheres, supporting observations [2,9] that the surface of Venus is oxidized.

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